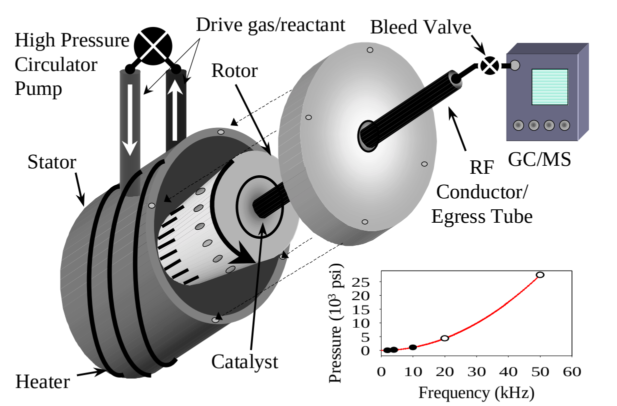
ARGONNE NATIONAL LABORATORY
Chemical Technology Division
New Solutions for Energy and the Environment
ENGINEERING | SCIENCE | INNOVATION

Rotational Exchange Gradient Imager Invention

Nuclear magnetic resonance (NMR) analysis is one of the most powerful tools available for the determination of chemical structures and reaction dynamics in homogeneous catalysis. We have invented a rotational exchange gradient imager that extends the capabilities of NMR to the study of heterogeneous catalytic reactions and the development of new materials and processes to make these reactions more efficient. This imager has diverse potential applications, including the development of improved fuel cells and processes for the petroleum and chemical industries.

The rotational exchange gradient imager makes use of magic angle spinning to narrow the broad NMR signals observed for solid samples. Other researchers have used magic angle spinning NMR to study heterogeneous catalyzed reactions at elevated pressures. Several technical problems, however, limit the use of this technique. For flow-through reactions, which include most industrial processes, the need for rotating seals limits attainable pressures to ~80 psi (~5.5 kPa). Glass, plastic, or ceramic pressure vessels are brittle and further limit pressures to less than 100 psi (6.9 kPa). Metal containers are thus necessary for the high pressures used in industrial applications, but they require that a radiofrequency (RF) detector coil be positioned inside the container. Enclosing the RF coil in a metal container complicates the apparatus significantly because the electromagnetic field generated by the RF coil strongly interacts with the electronically conductive surfaces. This electromagnetic interaction reduces the sensitivity of the detector. The device we have invented utilizes a metallic toroid cavity that circumvents the problem by combining the functions of the high-pressure container (up to 50,000 psi or 345 MPa) and the RF coil into one device.

The schematic below illustrates the operation of the rotational exchange gradient imager. The catalyst sample is contained in a ceramic rotor, which is propelled by a jet of gas containing the reactant(s), and rotated around the egress tube at a rate of 1-50 kHz. The stator is a toroid cavity resonator with the egress tube serving as its central conductor. A bleed-off valve and regulator maintain a reduced pressure in the egress tube and draw off the products of the reaction for analysis by gas chromatography, mass spectrometry, or other methods. The circulator pump drives the rotor and produces very high pressures.

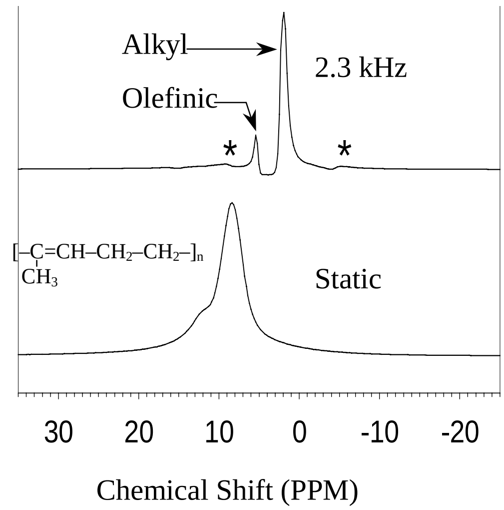


Schematic of the Rotational Exchange Gradient Imager. High-pressure carrier gas doped with reactant gases circulates in a closed loop and causes the turbine to rotate at up to 50 kHz. The axis of rotation is inclined at the magic angle (54.74°) with respect to the direction of a static external magnetic field.

The stator and central conductor tube generate the RF magnetic field for the NMR analysis. This design avoids the problem of a metal container interfering with the RF field because the container itself generates the RF field. This geometry has two other significant advantages over a conventional solenoid coil. First, the RF magnetic field is contained within the cavity, so that it can be generated more efficiently. The high efficiency increases the sensitivity of the imager. Second, the strength of the RF field decreases with distance from the center of the stator. As a result, the imager has the capability to record high-resolution NMR spectra for heterogeneous samples as a function of distance on a microscopic scale.

The figure on the right illustrates the ability of the imager to narrow NMR signals in a sample of poly(isoprene) for easy identification of the hydrocarbon species present. The broad spectrum observed for the static sample is narrowed and shifted upon rotation of the sample at 2.3 kHz. We were thus able to resolve two distinct peaks, corresponding to the alkyl (methyl and methylene) protons at 1.9 ppm and the olefinic protons at 5.4 ppm, in the approximate ratio of 7:1. The enhanced resolution of the different proton signals makes it possible to detect subtle changes in the conformations, dynamics, and packing of molecules subjected to large compressing forces.

The imager has application in tribology and rheology because of its ability to generate stresses in solids and semisolids via centrifugal forces. The centrifugal forces in our device can produce the pressures plotted in the figure on the preceding page (lower right), which were calculated for a 100-µm-thick annular shell of a polymer. As shown by the solid circles in this figure, our prototype apparatus can attain pressures of 200-1000 psi (1.4-6.9 MPa). The open circles project that stresses from pressures as high as 30,000 psi (207 MPa) can be obtained by using existing commercial rotors. Since stress inside the sample varies with distance from the center of rotation, a radial image of the NMR spectrum maps changes in the sample with respect to stress. A larger variation in stress can be obtained by increasing the rotation rate. In support of a program on development of a lithium-polymer battery, we plan to investigate the effect of polymer deformation for the range of stresses obtainable with our device.



Proton NMR Spectra of Polymer Obtained with the Rotational Exchange Gradient Imager at a Spin Rate of 0.0 and 2.3 kHz. The asterisks (*) indicate the location of spinning side bands.

ANL Participants

Rex E. Gerald II, Robert J. Klingler, and Jerome W. Rathke. For further information contact Rex E. Gerald II at (630) 252-4214 or gerald@cmt.anl.gov.